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# Optimized Performance of Quasi-Solid-State DSSC with PEO-Bismaleimide Polymer Blend Electrolytes Filled with a Novel Procedure

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Dye-sensitized solar cell (DSSC) is an attractive renewable energy technology currently under intense investigation. Electrolyte plays an important role in the photovoltaic performance of the DSSCs and many efforts have been contributed to study different kinds of electrolytes with various characteristics such as liquid electrolytes, polymer electrolytes and so on. In this study, DSSC is developed by using quasi-solid electrolyte and a novel procedure is adopted for filling this electrolyte. The quasi-solid-state electrolyte was prepared by mixing Poly ethylene oxide (PEO) and bismaleimide together and constitution was taken as PEO (15 wt%) at various bismaleimide concentrations (1, 3, 5 wt%). The novel procedure of filling electrolyte consists of three major steps (first step: filling liquid electrolyte, second step: vaporization of liquid electrolyte, third step: refilling quasi-solid-state electrolyte). The electrochemical and photovoltaic performances of DSSCs with these electrolytes were also investigated. The electrochemical impedance spectroscopy (EIS) indicated that $TiO_2$/Dye/electrolyte impedance is reduced and electron lifetime is increased, and consequently efficiency of cell has been improved after using this novel procedure. The photovoltaic power conversion efficiency of 6.39% has been achieved under AM 1.5 simulated sunlight (100 W/cm$^2$) through this novel procedure and by using specified blend of polymers.

**Keywords:** DSSC, Quasi-Solid-State, Electrolyte, Photovoltaic Characteristics, Bismaleimide.

## 1. INTRODUCTION

The ever-increasing energy demands and concerns over climate change are motivating scientists to tackle present and future energy challenges. Fossil fuels have been the major energy source until the industrial revolution but the unbalancing of eco-system and limited supply are the major drawbacks due to which scientists and research groups are trying to find alternative energy resources. Photovoltaic is a promising renewable energy technology that converts sunlight to electricity and it will contribute significantly to solve the future energy problems of whole mankind.

Dye-sensitized solar cells (DSSCs) are considered to be a promising green technology capable of meeting our future energy demands. The unique design of DSSC offers a wide range of choices for its components, such as nanocrystalline metal oxides, photosensitizers, counter electrode materials, redox mediators and electrolytes. Owing to its ease of fabrication, wide application and cost-effectiveness, intensive research work on DSSCs has been carried out for over 20 years.[1–3] Although DSSCs based on liquid-state electrolytes have already achieved a record conversion efficiency of 11%[4] but there are some obstacles which limit its practical use. Some of problems are leakage of liquid electrolyte, volatilization of organic solvents and long-lasting durability. In order to solve these problems, many research groups have been succeeded to supersede the liquid electrolytes with gel-states or quasi-solid-state electrolytes,[5,6] such as organic hole transfer conducting polymers,[7] polymer gel electrolytes,[8,9] ionic liquid based electrolytes,[10,11] plastic crystal electrolytes,[12,13] and liquid electrolytes solidified with physically cross-linked gelators.[14] Quasi-solid-state electrolytes are considered as better substitute of liquid electrolytes due to their high ionic conductivity, good interfacial filling properties and relatively long term stability.[15] However, the conversion efficiencies of quasi-solid-state DSSCs are about ~4% in

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most cases while DSSC based on liquid electrolytes have reached as high as 11%. Quasi-solid electrolyte is viscous and cannot penetrate easily into the mesopores of the $TiO_2$ photoanode film. The mesoporous structure makes it especially difficult for the polymer to transport due to the viscosity and steric effect.[16] Gel electrolytes based on a polymer host such as PEO are also common and lot of examples can be found in literature. Gel electrolytes provide good ionic conductivities close to 1 $mS \cdot cm^{-1}$; however, the mechanical properties are poor. One alternative is to blend bismaleimide to the gel electrolyte to promote mechanical stability.

In this study, we focused on mechanical properties and stability of Gel electrolytes, for which polymer blend of poly-ethylene oxide (PEO) and 1, 1′-(methylenedi-4,1-phenylene) bismaleimide, commonly known as bismaleimide (polymerized on heating via condensation reaction)[17–19] was prepared for quasi-solid state DSSCs. The effect of blending the PEO and bismaleimide on the cell performance was investigated and the ratio was optimized. To further improve the cell performance; a three step novel procedure of filling electrolyte was adopted.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

Anatase $TiO_2$ particles (Ti-Nanoxide), Titanium (IV) chloride, Chloroplatinic acid hexahdrate, 1-butyl-3-methylimidazolium iodide (BMII), iodine ($I_2$), Lithium iodide (LiI), 4-tert-butylpyridine (TBP), Propylene carbonate (PC), acetonitrile, 1,1-(methylenedi-4,1 phenylene) bismaleimide and Poly(ethylene oxide) (average $M_w \sim 10{,}000$) were all purchased from Sigma Aldrich Co. and used as received (A.R. grade). FTO glass (2.2 mm, 8 $\Omega/cm^2$, Pilkington) was used as substrates in photoelectrode and counter electrode. N719 dye (Ru (LL-$(NCS)_2$), $L$ = 2,2-bipyridyl-4,4-dicarboxylic acid, $L$ = 2,2-bypyridyl-4,4-ditetrabutylalmmomium-carboxylate, Solaronix Co.) was used as a sensitized dye and Surlyn (60 $\mu$m, Dupont Co.) was used as spacer.

### 2.2. Preparation of Liquid and Polymer Electrolytes

The composition of liquid electrolyte is as follows: 0.6 M BMII, 0.05 M $I_2$, 0.5 M TBP, LiI 0.1 M in ACN and PC (6:4 in v/v). Qusai-solid electrolyte was prepared by adding 15 wt% of PEO and different wt% (0, 1, 3 and 5) Bismaleimide (BMI) into the Polypropylene carbonate (PC) solvent. Electrolyte based on PEO-Bismaleimide blend was optimized. Figure 1 shows photographs of PEO only (used in Cell-A) and PEO-BMI polymer blend (used in Cell-B, Cell-C and Cell-D) quasi-solid electrolytes. To improve efficiency, a three-step filling process was developed as shown in Figure 2. First we filled the liquid electrolyte for 24 hours and kept at room temperature and then this liquid electrolyte was vaporized in vacuum oven at 50 °C. Some remnants of liquid electrolyte having high boiling point remained inside the cell. At last, quasi-solid electrolytes were filled in the cells again.

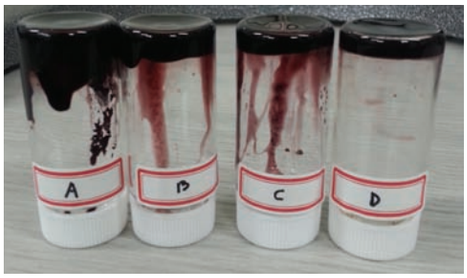


**Figure 1.** Photographs of PEO and PEO-bismaleimide blend polymer electrolyte: (A) Only PEO (15 wt%); (B) PEO-bismaleimide blend (15 and 1 wt% respectively); (C) PEO-bismaleimide blend (15 and 3 wt% respectively); (D) PEO-bismaleimide blend (15 and 5 wt% respectively).

### 2.3. Preparation of Working Electrode

Pre-washed FTO glass (1.5 ~ 1.5) was immersed in 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 minutes and then heated at 500 °C for 10 minutes. A transparent layer of anatase $TiO_2$ particles (Ti-Nanoxide) was pasted on the FTO glass by using doctor blade printing method, after then dried at room temperature for 30 minutes. After the printing, the FTO glass with $TiO_2$ paste was heated sequently in four steps of 325 °C, 375 °C, 450 °C and 500 °C for 5, 5, 15 and 15 minutes respectively using the high temperature furnace (Lab house Co.). The $TiO_2$ electrode was treated again with 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 minutes and then heated at 500 °C for 30 minutes to reduce the grain boundary. After cooling the substrate down at 80 °C, the photoelectrode was immersed into the dye solution (0.3 mM N-719 dye in ethanol) and kept at room temperature for 24 hours to adsorb the dye completely on the $TiO_2$ surface.

### 2.4. Fabrication of DSSC

Photoelectrode immersed in N-719 dye was rinsed with ethanol to remove the remnants of non-adsorbed dye. Counter electrodes were prepared by dropping a 5 mM $H_2PtCl_6$ isopropanol based solution on pre-washed FTO glass with a hole to inject electrolyte and heated at 400 °C for 20 minutes. Photoanode and counter electrode were sandwiched with a surlyn using hot-presser at 120 °C for few seconds. After filling the electrolyte through the hole, the holes were covered with small squares of Surlyn and

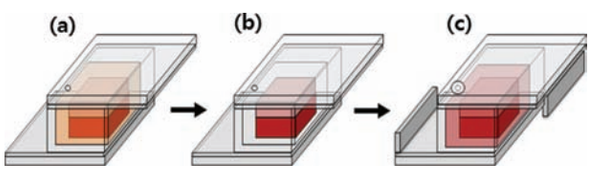


**Figure 2.** Diagrams of cells (a) liquid electrolyte injected, (b) liquid electrolyte vaporized and (c) quasi-solid electrolyte re-injected.

sealed completely with cover glass. A black mask of 25 ($5 \times 5$) mm$^2$ apertures was placed on the front electrode for better analysis of photovoltaic characteristics.[20]

### 2.5. Conductivity of Electrolyte

The total ionic conductivity is defined as follows:

$$\sigma = \frac{l}{|Z| \cdot A} \tag{1}$$

Where: $\sigma$ is the total conductivity $|Z|$ is the impedance, $l$ and A are the cell dimensions (length and area respectively). Individual ion transport is required to understand the influence of each ion on the cell performance. The total conductivity can also be expressed by the following equation:

$$\sigma = \sum_i |Z_i| F c_i \mu_i = \sum_i \frac{|Z_i|^2 F c_i e D_i}{K_B T} \tag{2}$$

Where: $Z_i$, $c_i$, $\mu_i$ and $D_i$ are the charge, concentration, mobility and the diffusion coefficient of ionic species respectively; $e$ is the electronic charge; $T$ is the absolute temperature; $K_B$ is the Boltzmann constant; $F$ is the Faraday's constant.[21]

### 2.6. Characterization



Photocurrent–voltage measurement was performed by using K101 Lab20 (PolaronixCo.) source measuring unit. Solar simulator with 160 W Xenon arc lamp was used as light source satisfying AAA class (spectral match; 0.75~1.25, non-uniformity of irradiance; $\leq \pm 2\%$, temporal instability; $\leq \pm 2\%$). The light intensity was calibrated with a KIER-calibrated Si solar cell (Mc science Co.). Electrochemical impedance spectrum of the cell was observed using frequency range of 0.05 Hz to 50 MHz under 100 mW/cm$^2$ using ultimate electrochemical workstation (BioLogic Co.).

The ion conductivities of the electrolytes were measured using a lab-made four-point probe conductivity cell connected to an impedance analyzer (BioLogic Co.).

## 3. RESULTS AND DISCUSSION

The variation in the viscosity of electrolyte by changing the wt% of bismaleimide could be clearly observed by the photographs shown in Figure 1. The electrolyte turns to solid state in less than 10 hours at room temperature on blending appropriate amount of the PEO and bismaleimide. The solidification of electrolyte increases on increasing the bismaleimide weight percentage.

Figures 3(a) and (b) show the photocurrent density-voltage curve for DSSCs fabricated using one-step filling procedure and novel three step filling procedure based on various bimaleimide concentrations under the illumination of simulated AM 1.5 solar light (100 mW/cm$^2$). On the

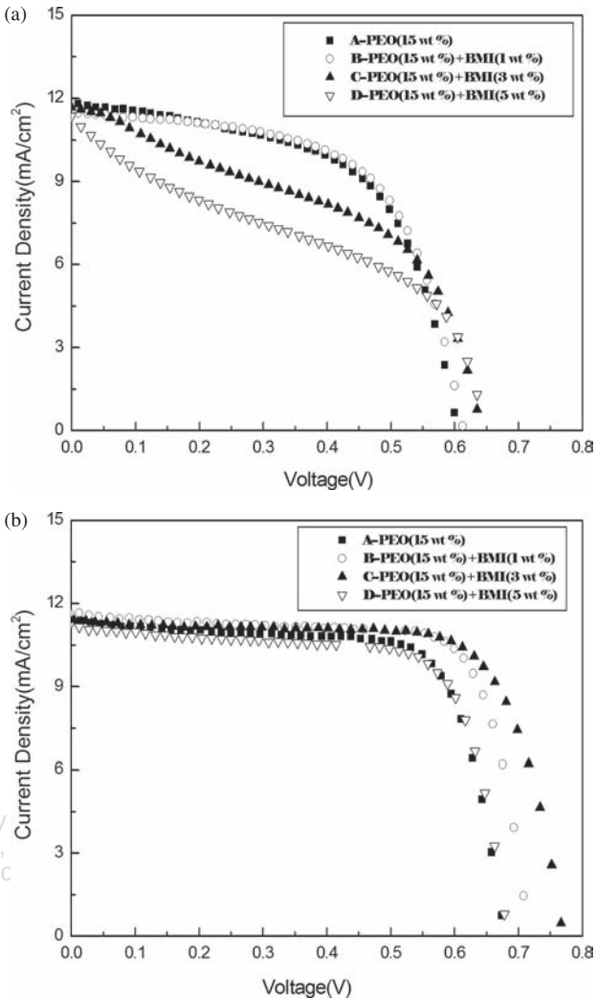


**Figure 3.** The photocurrent density-voltage curves of the DSSCs fabricated with quasi-solid electrolyte (a) one-step filling procedure and (b) Novel three step filling procedure.

basis of the current–voltage measurements, the cell efficiency ($\eta$) of each cell was calculated from open-circuit voltage ($V_{oc}$), short-circuit current ($J_{sc}$) and fill-factor (FF). In the case of only one-step electrolyte filling, the cell-A (only PEO 15%) yielded $J_{SC} = 11.75$ mA/cm$^2$, $V_{OC} =$ 610 mA, and $FF = 58.22$, corresponding to $\eta = 4.51$. Cell-B, cell-C and cell-D having bismaleimide wt% 1, 3 and 5 respectively, showed decreasing trend of cell efficiency (4.22%, 3.52% and 2.86% respectively). This is due to the decreasing trend of FF and conductivity of electrolyte as shown in Table I(a). On the other hand, the cells fabricated with our novel filling three step procedure showed improved results than former experiments as shown in Figure 3(b). The best photovoltaic performance is observed for cell-C having 3 wt% bismaleimide ($J_{SC} =$ 11.40, $V_{OC} = 0.75$, $FF = 72.77$ and $\eta = 6.39$). The photovoltaic performances are improved for all cases using new and novel filling procedure. The remarkable improvement

**Table Ia.** Photovoltaic performance of DSSC fabricated with one-step electrolyte filling procedure.

| | $V_{OC}$ [V] | $J_{SC}$ [mA/cm$^2$] | FF [%] | Eff [%] | $\sigma$ [S/cm] |
|---|---|---|---|---|---|
| PEO | 0.61 | 11.75 | 58.22 | 4.51 | 0.1107 |
| PEO + BMI (1 wt%) | 0.62 | 11.53 | 57.31 | 4.22 | 0.1065 |
| PEO + BMI (3 wt%) | 0.64 | 11.69 | 46.81 | 3.52 | 0.1028 |
| PEO + BMI (5 wt%) | 0.65 | 11.34 | 38.89 | 2.86 | 0.0901 |

**Table Ib.** Photovoltaic performance of DSSC fabricated with novel three step electrolyte filling procedure.

| | $V_{OC}$ [V] | $J_{SC}$ [mA/cm$^2$] | FF [%] | Eff [%] |
|---|---|---|---|---|
| PEO | 0.67 | 11.45 | 71.96 | 5.58 |
| PEO + BMI (1 wt%) | 0.71 | 11.66 | 71.48 | 5.98 |
| PEO + BMI (3 wt%) | 0.75 | 11.40 | 72.77 | 6.39 |
| PEO + BMI (5 wt%) | 0.68 | 11.19 | 70.90 | 5.10 |

is in FF of cells fabricated with novel filling procedure as can be seen in Tables I(a) and (b).

Electrochemical impedance spectroscopy (EIS) was used to characterize the internal/interfacial resistances of cell. $R_0$ in Figure 4(a) is the ohmic series resistance of the dye-sensitized solar cells, representing the electron transport processes with a very short time constant. The first semicircle ($R_{ct1}$) is the resistance at the interface of the Pt/electrolyte solution.[22] The second semicircle ($R_{ct2}$) represents the resistance component at the $TiO_2$/dye/electrolyte interfaces.[23] The third semicircle ($R_{ct3}$) represents Nernstian diffusion but there is no any significant relationship between $R_{ct3}$ and performance of the cell.[24] The impedance spectra displayed in Figure 4(a) and (b) shows three semicircles in the measuring frequency from 0.05 Hz to 50 MHz. The first semicircle ($R_{ct1}$) in Figure 4(a) is about same as in Figure 4(b), however, the novel filling procedure evidently reduces second semicircle ($R_{ct2}$) area, which results in the improvement of FF.

The cell with PEO (15 wt%) showed the highest efficiency of 4.51% among the cells with one-step filling electrolyte procedure, however the cell with blended electrolyte [PEO (15 wt%) and bismaleimide (3 wt%)] showed the highest efficiency of 6.39%. The dark impedance and Bode phase plots of cells were measured under forward bias in the dark to find the reason of better efficiency of cell-C. From the Bode phase plots shown in Figure 5(a), it is clear that the electron lifetime of the cell-C (bismaleimide 3 wt%) is much longer than that of the cell-A. The adsorbed polymers act as an insulating barrier to reduce the interfacial electron transfer rate ($k_{et}$) from the conduction band of $TiO_2$ to $I_3^-$ (dark current) and charge recombination at the dyed $TiO_2$ electrode/gel



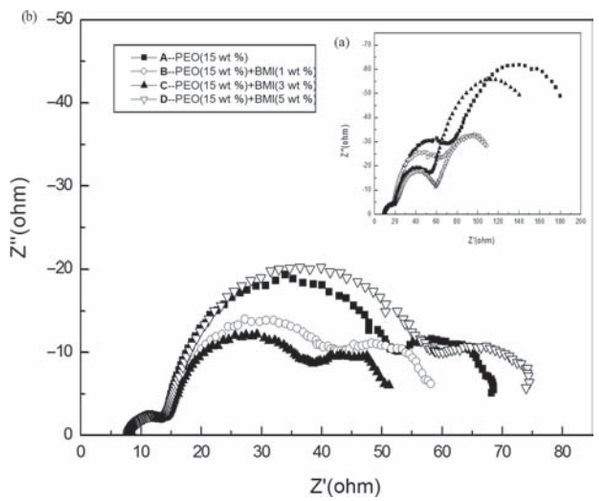


**Figure 4.** Electrochemical impedance spectrum (EIS) of cells with different electrolytes under simulated sunlight: (a) one-step filling procedure and (b) Novel three step filling procedure.

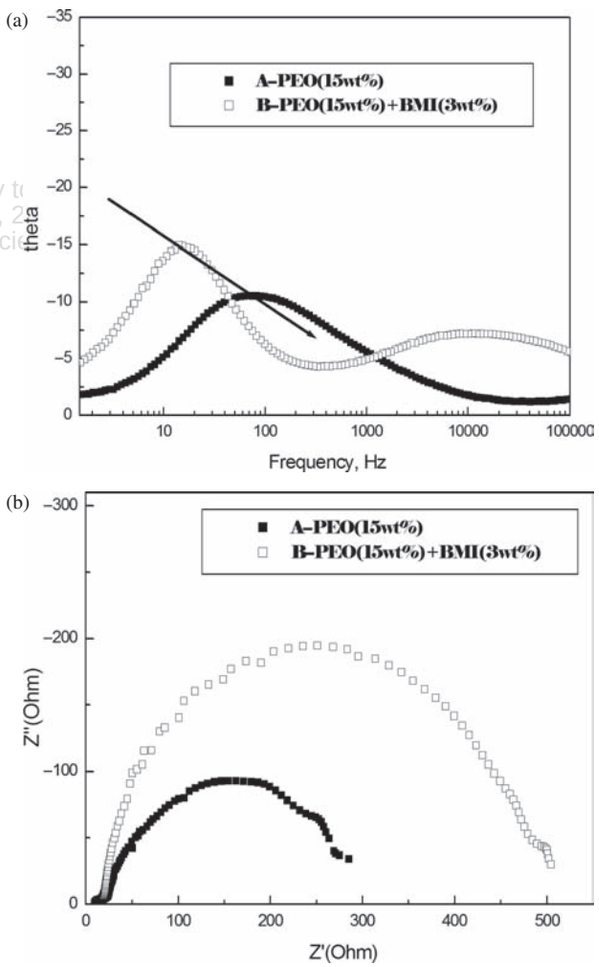


**Figure 5.** Dark Bode phase plots and Dark Impedance spectrum of cells with electrolyte having PEO only and PEO+bismaleimide: (a) Bode Phase Plots (b) Impedance spectrum.

electrolyte interface reduces[25–26] and as a result, $V_{oc}$ of cell increases. This is also consistent with the results of dark current measurement as shown in Figure 5. Generally $V_{oc}$ of quasi-solid-state electrolyte based devices is higher than liquid-state electrolyte based devices due to lower dark reaction (recombination) in quasi-solid-state electrolyte based devices. The interfacial impedance caused by the electron transfer from the conduction band of $TiO_2$ film to triiodide in the electrolyte could be described by the semicircle in intermediate-frequency region in the Nyquist plot.[27] Figure 5(b) shows the Nyquist diagram of the cells prepared by using a novel filling procedure. It is clear from the Figure 5(b) that the cell-C (bismaleimide 3 wt%) showed least interfacial impedance in intermediate-frequency region. It may be due to the slower recombination kinetics caused by the polymer matrix adsorbed on the $TiO_2$ surface and this matrix suppresses the back electron transfer from the $TiO_2$ film to the triiodide. Iodide is oxidized to triiodide at the counter electrode and the triiodide is diffused to the $TiO_2$ electrode to capture the electrons from the porous film at the $TiO_2$/dye/electrolyte interface.[23]

All the qusai-solid-state DSSC's showed similar $J_{SC}$ values. However, it is clearly evident that $V_{OC}$ is consistently increased with changing wt% of PEO-bismaleimide. This phenomenon could be understand from the following theoretical consideration:[28]

$$V_{oc} = \left[\frac{kT}{e}\right] \ln\left(\frac{I_{inj}}{n_{cb} k_{et} [I_3^-]}\right) \quad (3)$$



Where $k$ is the Boltzmann constant, $T$ is the absolute temperature, $e$ is the electronic elementary charge, $I_{inj}$ is the flux of electron injection from the dye molecules, $n_{cb}$ is the concentration of electrons at the conduction band of $TiO_2$/electrolyte interface, and $K_{et}$ is the rate constant for the back-electron-transfer reaction.

The photovoltage of a DSSC is kinetically limited by the back-electron-transfer reaction, where the electrons from the conduction band of $TiO_2$ recombine with the triiodide in the electrolyte.[29] Higher $V_{oc}$ of qusai-solid-state electrolyte is due to the additional function of the bismaleimide matrix which passivates the active $TiO_2$ surface and partly suppresses the dark reaction. It is reasonable to expect that the contact of the quasi-solid polymer with $TiO_2$ nanoparticle surface through the dissolution and diffusion of bismaleimide can alter the interfacial properties.

## 4. CONCLUSIONS

To enhance the performance of quasi-solid-state DSSC, this group optimized the constitution of quasi-solid-state electrolyte in DSSC and adopted a novel electrolyte filling procedure. In comparison of power conversion efficiency of different polymer-blend electrolytes [PEO, PEO + bismaleimide (1 wt%), PEO + bismaleimide (3 wt%) and PEO + bismaleimide (5 wt%)]; PEO + bismaleimide (3 wt%) using a novel electrolyte filling procedure yielded best power conversion efficiency of 6.39%. The cells fabricated with our novel three step filling procedure showed improved results than the cells fabricated with one step filling procedure. This was due to the improvement in FF and reduction in $TiO_2$/dye/electrolyte impedance. The decrease of back recombination has also given rise to the better $V_{oc}$. Finally all these results improved overall power conversion efficiency of quasi-solid-state DSSC. This new design having optimized blend of PEO + bismaleimide and novel filling procedure will be a concrete fundamental for the next generation quasi solid state dye sensitized solar cells.

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